

THE REARRANGEMENT OF METHANE AND METHYL CHLORIDE IN A MICROWAVE DISCHARGE

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I. INTRODUCTION

In a previous paper(1) the rearrangement of a series of hydrocarbons including methane in a microwave discharge was reported. The work reported here is an investigation of the effect of the introduction of a functional group in methane on the nature of both the gaseous and solid products of rearrangement. Such measurements should ultimately support a model of the rearrangement mechanism in a microwave discharge. Methane and methyl chloride were passed separately in the absence of a diluent through a microwave discharge.

II. EXPERIMENTAL

A. Materials

Methane (ultrahigh purity grade) was obtained from the Matheson Co. and used without further purification. The following analysis was supplied with the methane: CO_2 - <5 ppm; O_2 - 5 ppm; N_2 - 19 ppm; C_2H_6 - 14 ppm; C_3H_8 - <5 ppm. Methyl chloride (high purity grade) was obtained from the Matheson Co. and used without further purification.

B. Apparatus and Procedure

The rearrangements were carried out in a high vacuum flow system. The power source for the microwave discharge was a Raytheon generator (Model KV-174) and was operated at a power level corresponding to about 40 r.f. watts at 2450 Mc. The generator was connected to an air-cooled cavity (Raytheon - KV series) by a coaxial cable. Two procedures were used depending upon whether an analysis of the gaseous products was being made or whether solid film was being deposited for subsequent analysis. In the former case, the parent gas was passed through a variable leak valve (Veeco - VL). The pressure in a typical experimental run was 0.15 torr at a mass flow rate of 1×10^{-5} moles/min. and a linear flow rate of 20 cm./sec. In the latter case, the parent gas was passed through a Teflon needle valve (Fischer-Porter). The pressure in a typical experimental run was 0.50 torr. Normal deposition time was 20 min.

The gaseous rearrangement products of methane and methyl chloride were determined using a mass spectrometer (Associated Electronics Industries - MS-10). The sampling volume was located about 140 cm. downstream from the discharge. After establishment of a constant flow rate, the parent gas stream was sampled. An off-on valve upstream from the discharge allowed the system to

be pumped down without altering the setting of the variable leak. Between analyses pumpdown resulted in faster attainment of steady state concentrations of rearrangement products. Flow was again started and the discharge initiated with a Tesla coil. After establishment of a constant flow rate the discharged gas stream was sampled.

The solid polymeric films were removed mechanically from the walls of the Pyrex tubing. The infrared spectra of the films of both gases were obtained using either a Perkin-Elmer 421 or 621 spectrophotometer. The electron spin resonance spectra of the neat films from both gases were obtained on a Varian ESR 6 spectrometer. Elemental analyses of both films were made by Gailbraith Labs.

III. RESULTS

A. Gaseous Products

1. Mass spectra

Selected peaks from the mass spectra of methane and methyl chloride obtained with the discharge on and off are shown in Figures 1a and 1b. The most significant features in the methane spectra (Figure 1a) were the increase in the $m/e = 2$ (H_2^+) peak and the decrease in the $m/e = 15$ (CH_3^+) peak when methane was passed through the discharge. Trace quantities of higher molecular weight hydrocarbons were also noted. The most significant features of the methyl chloride spectra (Figure 1b) were the increase in the $m/e = 2$ (H_2^+) peak, the appearance of the $m/e = 30$ ($C_2H_6^+$) peak and the decrease in the $m/e = 50$ (CH_2Cl^+) peak when methyl chloride was passed through the discharge. Further, HCl was noted when the liquid nitrogen cooled trap downstream from the discharge was opened.

B. Solid Films

A solid film was observed to form in the discharge region when either methane or methyl chloride was passed through the discharge. Both films were characterized in several ways.

1. Elemental analysis

Empirical formulas for the solid films were established by elemental analysis. The formulas for the solid films formed from methane and methyl chloride were $(CH_{1.5})_x$ and $(CH_{0.65}Cl_{0.045})_x$, respectively.

2. Infrared spectra

The infrared spectrum of the film obtained from methane is shown in Figure 2 where a neat sample was used. Peaks ascribed to the film were noted in the region of the following frequencies: 2900, 1700, 1450, 1380 and 880 cm^{-1} . The assignments of these frequencies follow those given by Jesch et al (2). The band at 880 cm^{-1} may be due to rocking vibration of $-CH_3$ in a multiple carbon atom chain. The band at 1380 cm^{-1} is characteristic of $-CH_3$ deformation. The band at 1450 cm^{-1} is characteristic of $-CH_2$ symmetric scissors vibration. The band at 1700 cm^{-1} was probably due to carbonyl formed on exposure of the film to air. The 2900 cm^{-1} band

is due to C-H stretching vibration.

The infrared spectrum of the film obtained from methyl chloride is shown in Figure 3 where a neat sample was used. The low intensity peaks were a characteristic of the methyl chloride films whether run as a neat sample or as a KBr pellet. Peaks ascribed to the film were noted in the region of the following frequencies: 2900, 1700, 1580, 1440 and 875 cm^{-1} . The peak at 1380 cm^{-1} observed in the methane film is absent in the methyl chloride film and a new peak at 1580 cm^{-1} is observed in the methyl chloride film.

3. Electron spin resonance

The electron spin resonance spectra of the films produced from methane and methyl chloride are shown in Figures 4a and 4b. A significantly larger free spin concentration on the order of one thousand times greater was noted in the case of the methyl chloride film. No fine structure was observed in the case of the methyl chloride film. g-values for both films were essentially identical to the value for pitch ($g = 2.000$).

4. Solubility studies

An extensive series of liquids were tested as possible solvents for the films prior to NMR measurements. Solubility of the methane film was observed only in the case of hexamethylphosphamide and concd. H_2SO_4 .

IV. DISCUSSION

Investigations of chlorinated hydrocarbons in a microwave discharge have not been reported in the literature previously. Swift et al (3) however have investigated the effect of an rf discharge on CCl_4 in the absence of a diluent. A number of chlorinated gaseous products were reported in addition to a chlorinated polymer. The present work indicated a limited number of gaseous products. The results are consistent with the argument that molecules in a microwave discharge are subjected to a greater degree of fragmentation than in an rf discharge thereby limiting both the number and the complexity of gaseous products.

From the previous work of Vastola and Wightman (1) the following postulate could be advanced: if a parent hydrocarbon has a hydrogen to carbon (H/C) ratio greater than about 1.6, a hydrogen saturated solid film will be produced on passage of the hydrocarbon through a microwave discharge in addition to hydrogen. Conversely, if a parent hydrocarbon has a (H/C) ratio less than about 1.6 a hydrogen deficient film will be produced and no hydrogen will be observed.

The present work is an attempt to test the validity of this postulate if a functional group is introduced into the hydrocarbon molecule. Methyl chloride was chosen since it represents a straightforward extension of the methane case. Methyl chloride has a (H/C) ratio of 3 and if the Cl is neglected, the formation of a hydrogen saturated film would be predicted. However, HCl was observed as a rearrangement product. Hence the Cl can not be neglected and yet assuming the limiting case of a 1:1 correspondence between CH_3Cl and HCl, the (H/C) ratio of the remaining fragment would be 2. Thus the formation of a hydrogen saturated film would still be predicted but which in fact was not observed.

Instead a hydrogen deficient film was produced. The formation of a hydrogen deficient film from a parent molecule which has a high enough (H/C) ratio to form a hydrogen saturated film can be attributed to two factors. In the first instance, Cl preferentially appears in the gas phase as is indicated by the low percentage of Cl in the film, the absence of a significant C-Cl absorption peak in the infrared spectrum (Figure 3) and the presence of HCl downstream from the discharge. The extension of this work to other functional groups is anticipated to determine if this is a general scheme. In the second instance, the tendency to form hydrogen in a microwave discharge is again noted in the case of methyl chloride as in the case of methane (Figures 1a and 1b). Apparently for hydrocarbons containing functional groups, the formation of hydrogen is favored even at the expense of the formation of a hydrogen deficient film. The formation of ethane observed as a product of the methyl chloride discharge could be due to the recombination of methyl radicals produced in the discharge.

Films formed in various types of electrical discharges have not been extensively characterized. The recent work of Jesch et al (2) described the infrared analysis of a series of films produced from hydrocarbons in a glow discharge. Direct comparison between the present results and those of Jesch et al is not possible since two different types of electrical discharges were used. The type of discharge used dramatically alters the nature of both the gaseous and solid rearrangement products as indicated above.

The properties of the film produced from methyl chloride are similar to those reported previously (1) for the hydrogen deficient films formed from acetylene, benzene and naphthalene. The color of the methyl chloride film was dark (brownish-black) characteristic of hydrogen deficient films in contrast to the light yellow methane film characteristic of hydrogen saturated films. The high electron spin concentration of the methyl chloride film had also been observed for the hydrogen deficient film from acetylene.

The films produced from both methane and methyl chloride appear to be highly cross-linked as evidenced by the negligible solubility in liquids used as solvents for other polymeric systems. The methyl chloride film contains a greater number of free electrons than the methane film indicative of a significant number of unsaturated valences in the methyl chloride film. The methyl chloride film appears to be characterized by a greater degree of unsaturation than the methane film. Highly unsaturated polymeric systems have been found difficult to analyze by infrared spectroscopy* which has also been noted in the present results. Definitive NMR work would be helpful in elucidating the nature of these polymeric films.

* private communication with Dr. Vernon Bell (NASA - Langley Research Center)

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REFERENCES

- (1). F. J. Vastola and J. P. Wightman, J. Appl. Chem., 14, 69 (1964).
- (2). K. Jesch, J. E. Bloor and P. L. Kronick, J. Poly. Sci. A-1, 4, 1487 (1966).
- (3). E. Swift, Jr., R. L. Sung, J. Doyle and J. K. Stille, J. Org. Chem., 30, 3114 (1965).

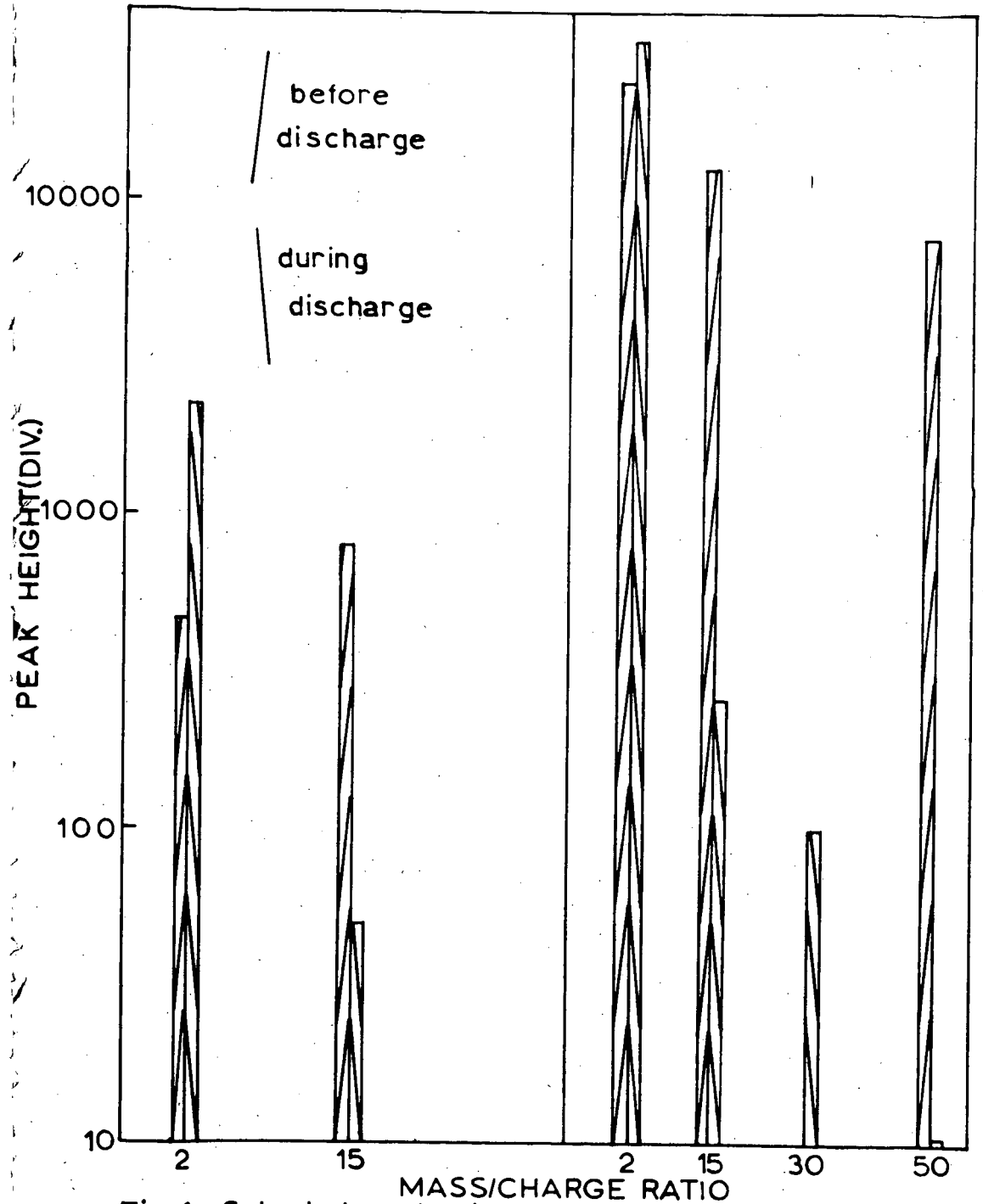
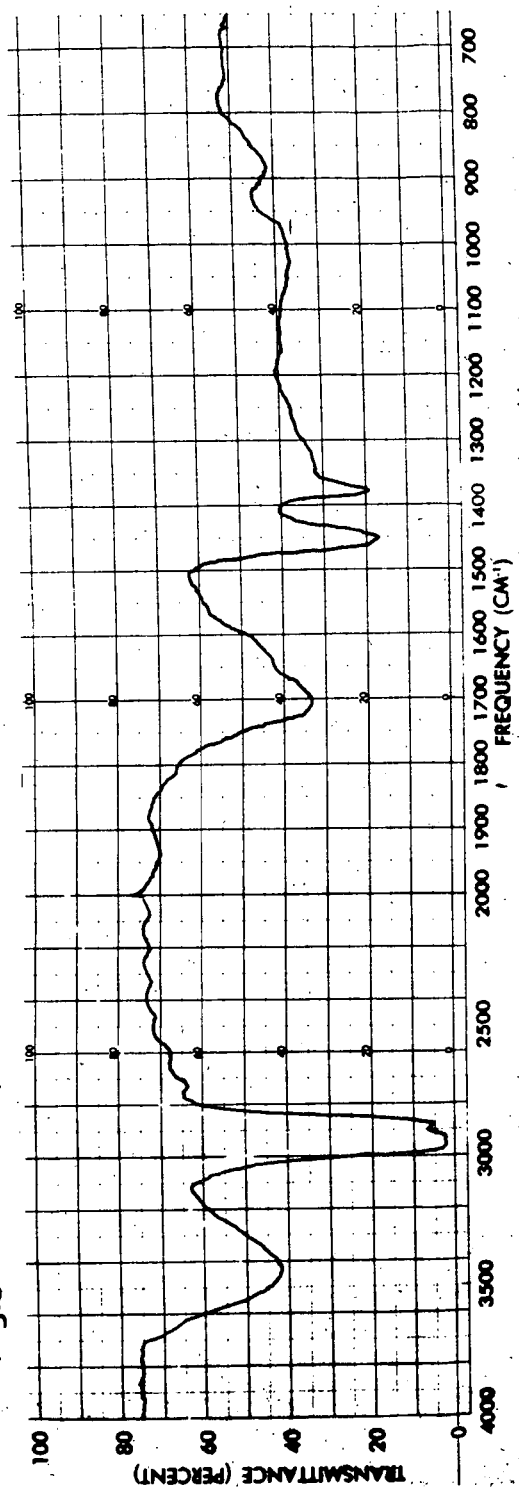
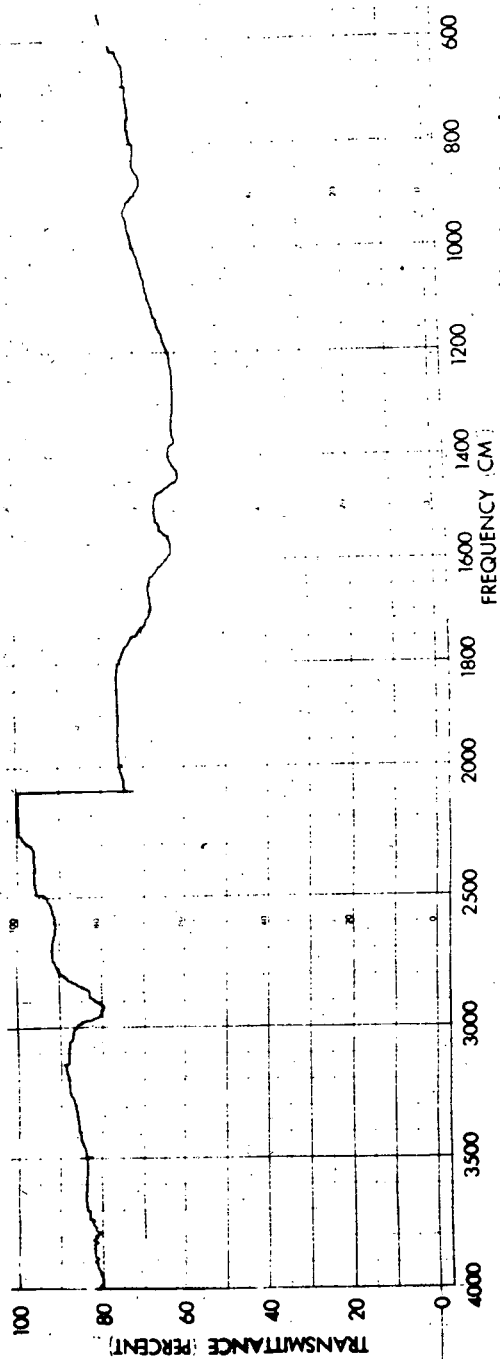


Fig.1a. Selected peaks from mass spectra of methane in a microwave discharge. Fig.1b. Selected peaks from mass spectra of methyl chloride in a discharge.



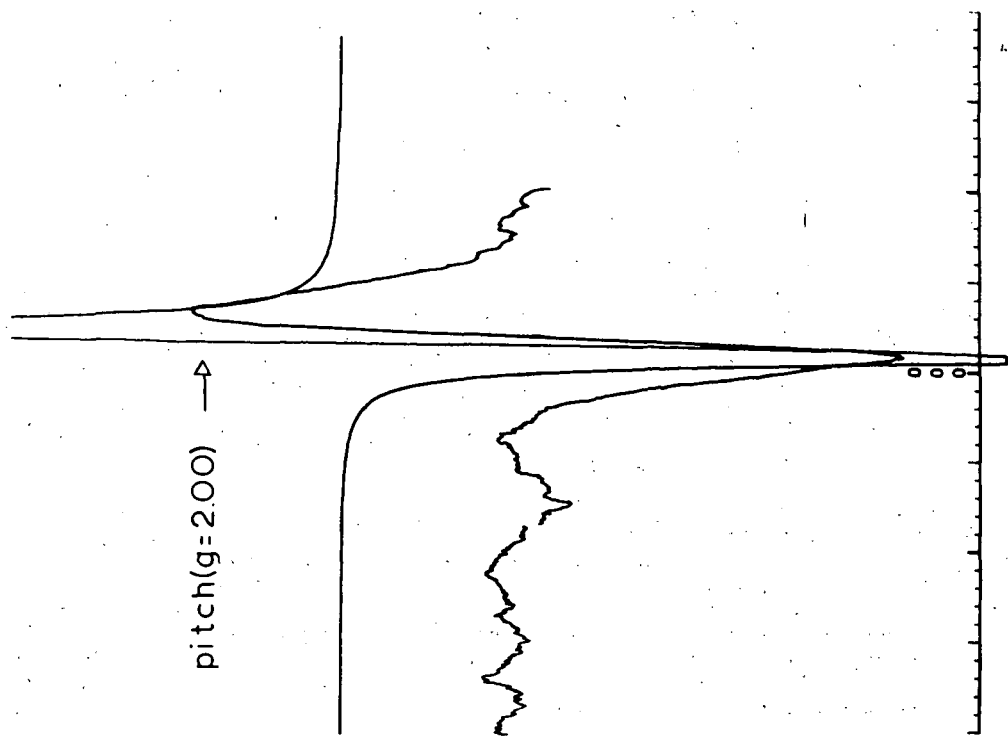


Fig.4a. ESR spectrum of polymer produced from methane.

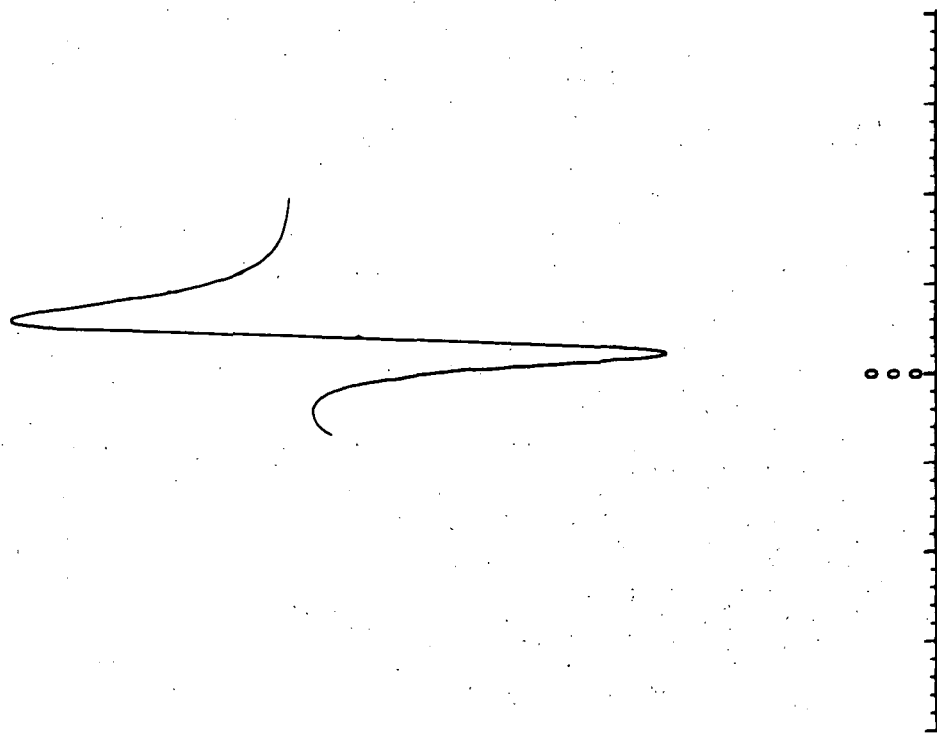


Fig.4b. ESR spectrum of polymer produced from methyl chloride.